Parafransoletite, a new dimorph of fransoletite from the Tip Top Pegmatite, Custer, South Dakota

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ABSTRACT

Parafransoletite, $Ca_3Be_2(PO_4)_2(PO_3OH)_2 \cdot 4H_2O$, is a triclinic dimorph of fransoletite from the Tip Top Pegmatite near Custer, South Dakota. Cell parameters are $a = 7.327(1)$ Å, $b = 7.696(1)$ Å, $c = 7.061(1)$ Å, $\alpha = 94.903(5)°$, $\beta = 96.820(5)°$, $\gamma = 101.865(5)°$, and $Z = 1$; space group $P\bar{1}$. The strongest X-ray powder diffraction lines are [d in Å (I)(hkl)] 3.032(100)(201,1$\bar{1}$2,11$\bar{2}$,2$\bar{1}$1), 3.619(80)(111), 2.595(60)(112), 7.52(50)(010), 2.334(40)(220, 30$\bar{1}$).

Parafransoletite is a secondary mineral found on fracture surfaces in beryl along with roscherite, montgomeryite, robertsite, mitridatite, whitlockite, and englishite. It occurs as colorless to white spear-shaped blades up to $0.4 \times 0.1 \times 0.04$ mm, as sheaf- and bow tie-like aggregates, and as compact radial sprays to 2 mm in diameter. Individual crystals are flattened on {010}, elongate ‖ [100], and exhibit the forms {010}, {011}, {13$\bar{1}$}, {$\bar{1}$31}, and {14$\bar{4}$}. The luster is vitreous for individual crystals, silky for aggregates. The Mohs hardness is about 2½, and no cleavage was observed. The density is 2.54(1) g/cm³ (meas), 2.56 g/cm³ (calc). Optically, the mineral is biaxial positive with $\alpha = 1.562(2)$, $\beta = 1.564(2)$, $\gamma = 1.588(2)$; Euler angles are $\phi = 98°$, $\theta = 85°$, $\psi = -13°$; $2V$ (calc) = 33°.

Parafransoletite, like most beryllophosphate minerals, results from the reaction of beryl with P-bearing hydrothermal solutions. The formation of these minerals is probably highly dependent upon pH.

INTRODUCTION

In terms of species diversity, the Tip Top Pegmatite is one of the world's most prolific sources of phosphate minerals. To date, at least 57 distinct phosphate species are known from the deposit, including 11 new species: ehrleite, fransoletite, jahnsite-(CaMnMg), parafransoletite (this study), pararobertsite, robertsite, segelerite, tinsleyite, tiptopite, and whiteite-(CaMnMg). Of these, five are beryllosphosphates: ehrleite, fransoletite, pahasapaite, parafransoletite, and tiptopite. Three other beryllophosphates hurlbutite, hydroxylherderite, and roscherite, have also been found at this locality, thus accounting for eight of the 19 known beryllophosphate minerals. At the Tip Top mine all eight occur along fracture surfaces in beryl crystals removed during the early 1980s.

In 1986 Martin Jensen sent the senior author four specimens that he collected at the Tip Top Pegmatite in October, 1983. Martin Jensen had performed preliminary X-ray powder diffraction, X-ray fluorescence, atomic absorption, and EDX studies on one of the minerals on these specimens, leading him to believe it to be a new calcium beryllium phosphate mineral. The powder pattern of the mineral was subsequently found to be very similar to that of fransoletite; however, because of obvious morphological differences between this mineral and fransoletite, detailed microprobe and single-crystal X-ray diffraction studies were undertaken. These showed the mineral to be a triclinic dimorph of fransoletite.

The mineral has been named parafransoletite for its dimorphic relationship to fransoletite. The mineral and name have been approved by the Commission on New Minerals and Mineral Names, IMA. The four specimens noted above can be reassembled into a single specimen, which is designated as the holotype specimen. Three fragments are deposited in the mineral collection of the Natural History Museum of Los Angeles County (LACMNH no. 35696), and one is in the mineral collection of the Smithsonian Institution, Washington, DC (NMNH no. 168432).

OCCURRENCE

Parafransoletite occurs in the Tip Top Pegmatite, located in the Black Hills, 200 m southwest of the center of Section 8, T4S, R4E (Fourmile quadrangle) and ap-

proximately 8.5 km southwest of Custer, Custer County, South Dakota. It was found with a variety of other secondary phosphates covering fracture surfaces in large beryl crystals from the outer-intermediate zone of the pegmatite. The mineral has been found in two different associations.

The holotype specimen was collected from one end of a large fractured beryl crystal, which later produced the secondary phosphate association designated by Campbell and Roberts (1986) as Phosphate Suite V (M. Jensen, personal communication, 1986). The mineral association on the holotype is generally consistent with the description of this suite provided by those authors. Mitridatite covers two opposing beryl fracture surfaces, having initially formed as dark red-brown, lamellar aggregates and later as botryoidal coatings in varying shades of olive-green and red-brown. Druses of colorless whitlockite rhombohedra postdate the lamellar mitridatite and predate at least some of the botryoidal mitridatite. Yellow transparent tablets of roscherite are locally present, having overgrown both whitlockite and botryoidal mitridatite. Colorless aggregates of tiny, pearly, montgomeryite blades are sparsely distributed on the botryoidal mitridatite. Parafransoletite has grown on top of the botryoidal mitridatite and the whitlockite druses, indicating that it is one of the last minerals to form in the assemblage.

A second specimen was provided by the Black Hills Institute of Geological Research, Inc. On one fracture surface of this beryl fragment parafransoletite is found in an association of minerals that is most consistent with that designated by Campbell and Roberts (1986) as Phosphate Suite IV. The parafransoletite crystals on this specimen are generally larger and more plentiful than on the holotype sample. Parafransoletite is the last mineral formed in a sequence that includes (from early to late) translucent colorless spherules of hurlbutite, yellow to red-brown rosettes of roscherite, large sprays of yellow to salmon-colored montgomeryite, dark red-brown balls of robertsite, and on one end a light olive-green to red-brown coating of mitridatite. An opposing surface of the same specimen exhibits a similar mineral association that is completely coated with mitridatite and devoid of parafransoletite.

PHYSICAL PROPERTIES

Individual parafransoletite crystals are transparent and colorless with vitreous luster and brittle, even fracture. Radial aggregates and subparallel crystal intergrowths are translucent white with a silky luster and an uneven fracture. The streak is white. The mineral does not fluoresce in ultraviolet radiation. The Mohs hardness is approximately 2½. Parafransoletite dissolves readily in cold 1:1 HCl.

The density, determined by the method of sink-float in a liquid mixture (tetrabromoethane and ethanol), is 2.54(1) g/cm³. The density calculated from the chemical and crystallographic data is 2.56 g/cm³.

OPTICAL PROPERTIES

An individual parafransoletite crystal was oriented by the precession X-ray method prior to the determination of its optical properties, which were determined on a Supper spindle stage using techniques described by Bloss (1981).

Parafransoletite is biaxial positive. The indices of refraction are $\alpha = 1.562(2)$, $\beta = 1.564(2)$, $\gamma = 1.588(2)$. The vibration directions are very approximately parallel to the crystallographic axes: $X \simeq \mathbf{a}$, $Y \simeq \mathbf{b}$, $Z \simeq \mathbf{c}$. The Euler angles are $\phi = 98°$, $\theta = 85°$, $\psi = -13°$. Because of the small size of parafransoletite crystals and their marked flattening approximately parallel to the acute bisectrix, $2V$ could not be measured and dispersion could not be observed. The optic angle $(2V)$ calculated from the indices of refraction is 33°.

MORPHOLOGICAL CRYSTALLOGRAPHY

Parafransoletite occurs as thin individual spear-shaped blades up to 0.4 × 0.1 × 0.04 mm, as sheaf- and bow tie–like aggregates, and as compact radial sprays to 2 mm in diameter. It is similar to collinsite in appearance and notably distinct from fransoletite (compare Fig. 1 in Peacor et al., 1983).

Most crystals are composite with slightly rounded faces tapering to a pointed termination. Individual crystals are flattened on {010} and elongate parallel to [100]. The forms, as determined by measurements on an optical goniometer, are {010}, {011}, {13$\bar{1}$}, {$\bar{1}$31}, and {14$\bar{4}$} as shown in Figure 1. Doubly terminated crystals are common and seemingly exhibit centrosymmetric development of crystal forms. Simple contact twinning on {010} is common.

X-RAY CRYSTALLOGRAPHY

X-ray precession photographs show parafransoletite to be triclinic. The cell parameters refined from four-circle diffractometer data are $a = 7.327(1)$ Å, $b = 7.696(1)$ Å, $c = 7.061(1)$ Å, $\alpha = 94.903(5)°$, $\beta = 96.820(5)°$, $\gamma = 101.865(5)°$. Crystal morphology is consistent with space group $P\bar{1}$, and subsequent structure determination (Kampf, 1992) proved this to be the correct space group.

Because of similarities with the monoclinic cell of fransoletite reported by Peacor et al. (1983) ($P2_1/a$, $a = 7.354$ Å, $b = 15.07$ Å, $c = 7.055$ Å, $\beta = 96.41°$, $V = 777$ Å³, $Z = 2$), the possibility that parafransoletite is untwinned fransoletite was carefully considered. Comparative X-ray precession photographs (MoKα radiation) of parafransoletite and type fransoletite were taken using the same camera. Precession photographs (MoKα) of fransoletite that were used in the original description of fransoletite were also obtained from D. R. Peacor for comparison. The $h0l$ planes of the two minerals coincide, but there are very few similarities in intensities. The intensity differences in this plane cannot be explained by a twin relationship. A parafransoletite precession exposure oriented to correspond to the $hk0$ plane in fransoletite exhibited

no correlation with the fransoletite lattice (except the co-incidence of the **a*** axes). No twinning of the parafran-soletite lattice could be devised that would yield the fran-soletite lattice. All peaks observed for parafransoletite were sharp and distinct; there were no diffuse peaks suggestive of an order-disorder relationship with fransoletite. In ad-dition, optical study of type fransoletite shows no evi-dence of twinning.

Several individual parafransoletite crystals were mounted in a Gandolfi camera for recording of the X-ray powder diffraction pattern. The observed and calculated powder data for fransoletite and parafransoletite are com-pared in Table 1. The two minerals yield very similar powder data. Nevertheless, distinct differences are obvi-ous, particularly when patterns obtained using the same camera are compared side by side. The differences in in-terplanar spacings and intensities indicated in the com-parative listing are significant and reproducible. The parafransoletite powder lines that are unique and distinct from those of fransoletite are not indexable using the fransoletite cell, and vice versa. Subsequent determina-tions of the atomic structures of fransoletite and parafran-soletite (Kampf, 1992) confirmed the conclusion that these are distinct species.

CHEMICAL COMPOSITION

Parafransoletite was analyzed for Ca and P using an electron microprobe with montgomeryite as a standard (the same montgomeryite standard was used in the elec-tron microprobe analysis of fransoletite by Peacor et al., 1983). Be was determined by induction-coupled plasma using a 21.8-mg sample and a sodium peroxide sinter. H_2O was determined by Karl Fischer titration on a Mit-subishi moisture titrator using a 10.89-mg sample. Mi-croprobe analyses on five points showed virtually no variation and yielded CaO 28.2 and P_2O_5 47.9; single Be and H_2O determinations yielded BeO 7.7 and H_2O 15.1; total 98.9 wt%. The empirical formula based upon 20 O atoms is $H_{2.05}Ca_{3.02}Be_{1.85}P_{4.05}O_{16}\cdot4H_2O$. The structure de-termination (Kampf, 1992) indicated that the simplified formula should be written $Ca_3Be_2(PO_4)_2(PO_3OH)_2\cdot4H_2O$, which requires BeO 8.45, CaO 28.41, P_2O_5 47.93, H_2O 15.21, total 100.00 wt%. This formula is identical to that of fransoletite.

The analysis by induction-coupled plasma yielded sig-nificant amounts of several other oxides: K_2O 0.47, MgO 0.17, FeO 0.55, Al_2O_3 0.09, and SiO_2 0.43. None of these oxides was detectable by the electron microprobe, and they are therefore best attributed to contaminants intro-duced during removal of parafransoletite crystals from their matrix. The low BeO value can be attributed in part to dilution by contaminants and in part to the uncertainty in the induction-coupled plasma analysis, estimated at about ±5% (0.4 wt% BeO).

The Gladstone-Dale compatibility index (Mandarino, 1981) for parafransoletite is −0.018. This indicates su-perior compatibility among the density, average index of refraction, and composition.
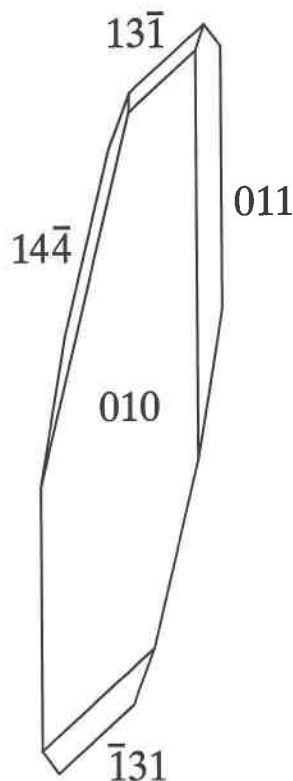

Fig. 1. Orthographic projection of parafransoletite.

COMMENTS ON THE OCCURRENCE OF BERYLLOPHOSPHATES

Of the 19 known beryllophosphate minerals (babef-phite, beryllonite, ehrleite, faheyite, fransoletite, gaine-site, glucine, herderite, hurlbutite, hydroxylherderite, moraesite, pahasapaite, parafransoletite, roscherite, tip-topite, uralolite, väyrynenite, weinebeneite, and zanaz-ziite), only hydroxylherderite and roscherite have been found at more than a handful of localities. Even where the other species do occur they are invariably rare. It is clear that the conditions necessary for the formation of beryllophosphate minerals must be very limited and spe-cific.

With the exception of babefphite and glucine, the ber-yllophosphates principally occur in pegmatites and usu-ally as the result of secondary hydrothermal alteration of beryl by solutions containing P derived from earlier formed minerals such as triphylite-lithiophilite. Perhaps significantly, 12 of the 18 beryllophosphates contain es-sential Ca, and this is true of seven of the eight known from the Tip Top Pegmatite. Five of the beryllophos-phates from the Tip Top Pegmatite (ehrleite, fransoletite, pahasapaite, tiptopite, and parafransoletite) have been found nowhere else. Interestingly, ehrleite, fransoletite, and parafransoletite have closely related structures based upon Be-P tetrahedral chains that are linked to one an-other by Ca (Kampf, 1992).

Considering that Ca, Be, and P are all relatively abun-

TABLE 1. X-ray powder diffraction data for fransoletite and parafransoletite

	Fransoletite					Parafransoletite			
hkl	I_{calc}	d_{calc}	I_{obs}	d_{obs}	hkl	I_{calc}	d_{calc}	I_{obs}	d_{obs}
020	67	7.5255	40	7.52	010	55	7.4830	50	7.52
001	9	7.0223	10	6.99	100	13	7.1003	10	7.04
110	30	6.5684	30	6.55	$1\bar{1}0$	17	5.8238	10	5.84
$11\bar{1}$	15	5.0621	20	5.06	$\bar{1}11$	28	4.5277	15	4.55
111	20	4.5700	30	4.57	$\bar{1}11$	22	4.4104	10	4.40
$12\bar{1}$	21	4.3740	30	4.38					
121	27	4.0447	—	—	111	99	3.6152	80	3.619
					$2\bar{1}0$	13	3.5184	15	3.482
131	100	3.4670	90	3.47	$20\bar{1}$	38	3.3587	20	3.360
$21\bar{1}$	52	3.3171	70	3.32	$12\bar{1}$	49	3.2891	20	3.293
					$21\bar{1}$	46	3.2542	20	3.249
$14\bar{1}$	15	3.0826			$2\bar{1}1$	10	3.0378		
211	19	3.0345	100	3.044	$11\bar{2}$	57	3.0378	100	3.032
$12\bar{2}$	63	3.0335			$1\bar{1}2$	17	3.0247		
					201	16	2.9979		
230	9	2.9517	10	2.958	$12\bar{1}$	12	2.9621	10	2.965
					$\bar{2}21$	10	2.7124	10	2.711
231	13	2.6360	10	2.640	$0\bar{2}2$	11	2.7064		
					112	28	2.5964		
132	33	2.5954	40	2.597	211	13	2.5830	60	2.595
					$12\bar{2}$	16	2.5713		
					030	9	2.4943		
$14\bar{2}$	15	2.4873	10	2.484	$12\bar{2}$	7	2.4886	25	2.485
					$\bar{1}2\bar{2}$	15	2.4743		
					$30\bar{1}$	12	2.3429		
250	40	2.3224	50	2.317	220	16	2.3337	40	2.334
					003	18	2.3218		
$16\bar{1}$	23	2.2732	10	2.273	$\bar{2}30$	38	2.2892	20	2.294
123	9	2.2053	10	2.201	$13\bar{1}$	30	2.1972	15	2.200
113	6	2.1371	10	2.139	301	11	2.1512	10	2.148
152	5	2.1365			$03\bar{2}$	8	2.1460		
					$3\bar{0}2$	7	2.0987	10	2.094
					$31\bar{2}$	3	2.0899		
					$\bar{3}30$	13	1.9412	10	1.938
203	14	1.8761	20	1.878	$21\bar{3}$	22	1.8660	25	1.870
$18\bar{1}$	10	1.7758	30	1.777					
					$32\bar{3}$	6	1.6635	10	1.664
					$\bar{2}04$	7	1.6577		
					$21\bar{4}$	6	1.6205	15	1.620
					$\bar{2}1\bar{4}$	6	1.6165		
290	6	1.5204	20	1.518	240	6	1.5236	20	1.521
$41\bar{3}$	2	1.5180			322	5	1.5198		
422	2	1.5172			$4\bar{2}2$	4	1.5189		
$24\bar{4}$	3	1.5167							
$37\bar{2}$	12	1.5081	10	1.508					

Note: Observed data for parafransoletite were obtained using a 114.6-mm Gandolfi camera, CuKα (Ni filtered) radiation (λ = 1.54178), visually estimated intensities. Observed data for fransoletite are from Peacor et al. (1983). Only observed lines for which $I \geq 10$ are listed. Calculated patterns were obtained using data from Kampf (1992).

dant in many pegmatites, the rarity of beryllophosphates might be attributed to several factors:

1. These minerals are all secondary in origin and require the freeing of Be and P from primary or intermediate secondary phases containing these cations.

2. The sources of remobilized P (most importantly triphylite-lithiophilite) and Be (most importantly beryl) are not often found in close proximity in pegmatites.

3. For the most part, beryllophosphates form at relatively low temperatures (>250 °C), and beryl is generally very resistant to alteration, especially at low temperatures.

4. The behavior of Be in aqueous solution is very sensitive to pH, and therefore it is likely that the beryllophosphates form over very narrow pH ranges.

Spurred in part by the discovery of zeolite-like structures for the minerals tiptopite and pahasapaite, Harvey and Meier (1989) successfully synthesized several framework beryllophosphates. They used a hydrothermal method with temperatures not unlike those assumed for secondary hydrothermal pegmatite processes. Their work confirms that pH is a critical factor in the formation of beryllophosphates. In particular, they noted that Be and P are both readily soluble in acidic solutions and that framework beryllophosphates are best produced at a pH around 6. At pH < 4 only small amounts of unspecified "dense" anhydrous beryllophosphates are produced, and at pH > 7 no crystalline beryllophosphates result. They also showed that the beryllophosphate framework formed is dependent upon the presence of a specific alkali cation

(Li, Na, K, Cs, or Na + K). The compound that they prepared using Li$^+$ is essentially the same as pahasapaite.

Unfortunately, the syntheses of Harvey and Meier were specifically designed to yield framework beryllophosphates. Components were adjusted so that Be/P = 1 (optimal for beryllophosphate frameworks), other cation systems were not considered, and the effects of varying concentration, temperature, and pressure were not studied. It is likely that solutions containing other proportions of Be and P and a variety of other cations, particularly Ca^{2+}, would yield other beryllophosphate structures over a similar range of pH and temperature. It also seems likely that the degree of condensation of Be and P tetrahedra in these compounds is dependent, in part, on pH and that less condensed structures might be expected at lower pH.

The beryllophosphate assemblages at the Tip Top Pegmatite are mineralogically and chemically complex. Trends in solution composition, pH, and temperature are difficult to interpret from the observed paragenetic sequences (such as those noted by Campbell and Roberts, 1986). This is particularly true because of the paucity of experimental evidence pertaining to the minerals involved and to their relative stabilities in these systems. Nevertheless, a consideration of only the beryllophosphates suggests that earlier phases (i.e., tiptopite and hurlbutite) tend to have more highly condensed structures and lower H$_2$O contents than do later phases (i.e., fransoletite, parafransoletite, and ehrleite). (Pahasapaite is an exception in that it is a late-formed mineral with a framework structure; however, it does have a high H$_2$O content.) This evidence suggests that pH and temperature decreased as these systems matured.

The dimorphs fransoletite and parafransoletite were the last to form in very similar assemblages, and there is little doubt that they formed under very similar conditions. The two minerals have not, however, been found on the same specimens, suggesting that there is some distinct difference in conditions that favors one over the other. The subtle differences between their structures fail to provide any clue to this puzzle.

REFERENCES CITED

Bloss, F.D. (1981) The spindle stage: Principles and practice, 340 p. Cambridge University Press, Cambridge, England.

Campbell, T.J., and Roberts, W.L. (1986) Phosphate minerals from the Tip Top mine, Black Hills, South Dakota. Mineralogical Record, 17, 237–254.

Harvey, G., and Meier, W.M. (1989) The synthesis of beryllophosphate zeolites. In P.A. Jacobs and R.A. van Santen, Eds., Zeolites: Facts, figures, future, p. 411–420. Elsevier, Amsterdam.

Kampf, A.R. (1992) Beryllophosphate chains in the structures of fransoletite, parafransoletite, and ehrleite and some general comments on beryllophosphate linkages. American Mineralogist, 77, 848–856.

Mandarino, J.A. (1981) The Gladstone-Dale relationship: Part IV. The compatibility concept and its application. Canadian Mineralogist, 19, 441–450.

Peacor, D.R., Dunn, P.J., Roberts, W.L., Campbell, T.J., and Newbury, D. (1983) Fransoletite, a new calcium beryllium phosphate from the Tip Top Pegmatite, Custer, South Dakota. Bulletin de Minéralogie, 106, 499–503.